

MRS Singapore – ICMAT Symposia Proceedings

8th International Conference on Materials for Advanced Technologies

**Investigation of Wettability Properties of Laser Surface
Modified Rare Earth Mg Alloy.**Khadka Indira^{a, b, *}, Castagne Sylvie^{a, b}, Wang Zhongke^{a, c}, Zheng Hongyu^{a, c}*a. SIMTech-NTU Joint Laboratory (Precision Machining), Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798**b. School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798,**c. Machining Technology Group, Singapore Institute of Manufacturing Technology, 71 Nanyang Drive, Singapore 638075***Abstract**

Mg and its alloys are used in various application areas, where the wetting property is a special requirement. For example, surface wettability of a biomaterial plays a vital role in cell adhesion and proliferation. In this context, rare earth Mg alloy (WE54), a potential biomaterial, was studied to examine its wetting behavior. In order to tailor the surface properties, laser surface melting (LSM), a single process method, was adopted. In this paper, the effective change on wettability properties of WE54 after LSM process was studied under deionized water and simulated body fluid. A 500 watt nanosecond pulse Nd:YAG laser having a wavelength of 1064 nm was used to modify surface properties. Microstructure and surface morphology were examined by scanning electron microscope and profilometer, respectively. Cellular structure and some buds were observed on the laser melted surface of WE54. Evaporation of Mg and enrichment of Y up to 12.10% and 13.43% were observed. The contact angle was reduced from 81° to 41.03° in deionized water after laser treatment, whereas in SBF solution it was reduced to 23.13°. It indicates that WE54 alloy also has a bio-wettability characteristic, which is very important for bio-applications.

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Selection and/or peer-review under responsibility of the scientific committee of Symposium 2015 ICMAT

Keywords: Laser surface melting; WE54 alloy; Wettability; Contact angle; Surface roughness

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1. Introduction

Laser surface engineering is a promising approach for the surface modification of different materials. The high energy laser beam is capable to generate rapid rates of heating and cooling. The process can lead to a non-equilibrium cooling resulting in grain refinement, morphology change, phase transformation and change in chemical composition of surface without changing the properties of the bulk material. Compared to the other surface modification techniques such as sand blasting and machining, laser surface processing is a direct process which provides uniform surface structure. Unlike the coating method, laser processing does not have issue of poor adherence of surface with bulk material. In the past, laser technology has been used to improve surface properties such as mechanical, corrosion, wear and wettability properties of materials. Several researches have been reported concerning the efficiency of laser material processing to achieve better surface properties [1-3]. The wetting characteristics of a material can be modified efficiently by using proper laser processing parameters.

Lawrence et al. studied the wettability characteristics of different materials such as titanium and mild steel by using different types of lasers to modify the surfaces and liquids to evaluate wettability [1, 4]. The effective changes were found on wetting properties of mild steel by the use of lasers having different wavelength such as CO₂, Nd:YAG, excimer and high power diode laser [1]. Hao et al. have reported change in wettability characteristics of bio-grade stainless steel when kept in contact with simulated physiological liquids [3]. The adhesion properties of bio-grade stainless steel were improved after laser irradiation in SBF (simulated body fluid) and SBF with albumin fluid. Zhao et al. have used pulsed Nd:YAG laser to improve the wetting characteristics of copper [5]. They mentioned that the relative surface energy of Cu was improved as compared to that of as-received Cu, when the surface was irradiated by 1500W and 2000W laser power. The contact angle decreased from 42° to 31° in 2000W laser treated surface of Cu as compared to that of as-received Cu. Some researches have been reported on Mg-Al alloys concerning the improvement of wetting characteristics after laser irradiation. Guan et al. have reported the significant improvement in surface energy of laser melted AZ91D from 25.80 to 40.76 mJ/m² [6]. The formation of continuous network of β phase at the dendrite / cellular structure and the enrichment of Al cause the improvement in the corrosion and wettability properties. Demir et al. studied the wettability of laser structured AZ31 Mg alloy in water [7]. They concluded that the oxidized surface has a tendency to reduce the contact angle, while laser structured surface with entrapped air has a tendency to increase the contact angle. Ho et al. have reported the bio-wettability of AZ31B Mg alloy under SBF solution [8]. The enhancement of bio-wettability was due to the combined effect of surface roughness, grain size, surface morphology and surface chemistry. A surface with low roughness and homogenous chemical composition provides better bio-wettability. Enhancement in bio-wettability is necessary for the growth and activities of cell. Cell adhesion and proliferation highly depend upon the wetting characteristics of a biomaterial.

Mg as a potential bio-implant has drawn attraction of the researchers because of its physiological benefits [9, 10]. Mg alloys are recognized for their potential compatibility with human tissues due to their mechanical properties such as; Young's modulus and specific density which are close to human bone [14]. Therefore, they have minimum stress shielding effects as compared to the other biomaterials when they are used as a load bearing implant. The commercial Mg alloys AZ31 and AZ91 are potential biomaterials but the presence of Al causes negative impact on a human body. Studies have shown that Al induces allergic responses and immune disorders while experimented on rats [15]. The limitation of Mg-Al alloys encourages the further exploration on other types of Mg alloys. In this paper, high-potential biomaterial WE54 Mg alloy is studied. The wettability properties of the as-received and the laser modified WE54 Mg alloys under DI water and SBF solution were investigated. Microstructure, contact angle measurement, surface roughness and work of adhesion of WE54 alloy are reported in the following sections.

1.1. Contact angle and wettability

Young's equation: Thomas young (in 1805) has introduced the correlation between contact angle and interfacial tensions between solid, liquid and vapor at three phase equilibrium condition [16, 17], given by the Young's equation as follows:

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (1)$$

where, γ_{lv} , γ_{sv} , and γ_{sl} represent the liquid-vapor, solid-vapor, and solid-liquid interfacial tensions, respectively, and θ is the Young's contact angle. When the drop of liquid is in contact with the solid surface, the interfacial tensions and contact angle are linked through this equation. The contact angle is defined as the angle formed by the intersection of the liquid-solid interface and the liquid-vapor interface whereas the wettability is the ability of a solid surface to be in contact with liquid. The contact angle formed by the sessile drop on the smooth surface is shown in figure 1. The contact angle $\theta < 90^\circ$ indicates the better wetting properties, whereas $\theta > 90^\circ$ indicates less wetting of the surface. The surfaces that have contact angle larger than the 150° are referred as a super hydrophobic surface.

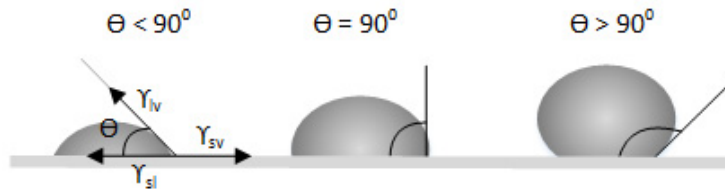


Figure 1: Contact angles formed by sessile liquid drops on a smooth surface, adapted from ref. [16]

The adhesion intensity of a liquid surface to a solid surface is known as work of adhesion, W_{ad} , and it can be calculated by the Young–Dupré equation:

$$W_{ad} = \gamma_{lv}(1 + \cos\theta) \quad (2)$$

By using equation (2), adhesion intensity of DI water and SBF solution can be calculated.

Surface roughness is one of the factors that greatly influence the wetting contact angle [6]. The correlation between roughness factor and contact angle θ , is described by Wenzel's equation. Wenzel's model represents the relationship between surface roughness and contact angle for homogenous surface. If the surface is heterogeneous then the Wenzel's model is not sufficient. Cassie/Baxter's model deals with the composite surface. It explains that the gas entrapped in the surface increase the contact angle. Cassie's model is mostly used for complex surfaces and super hydrophobic surface structures.

In this paper, the contact angle is the major parameter used to quantify the wettability of a surface. Surface roughness, chemical composition, oxygen content as well as surface chemistry are key factors that influence the wettability.

2. Experimental details

The material used in this study was an extruded WE54 alloy whose chemical composition is listed in table 1. The WE54 alloy was used for laser surface melting by pulsed Nd:YAG laser. The as-received WE54 bar of 3 cm diameter was cut into 3 mm thick disks. The samples were grounded from 320 to 2400 grit SiC paper before being subjected to ethanol cleaning and air flow drying. An etchant composed of 19 ml water, 60ml ethylene glycol, 20 ml acetic acid, 1 ml HNO_3 was used to etch the as-received and the laser melted surface of WE54 to reveal the microstructures. The etching time was 60 seconds.

Table 1: Chemical composition of WE54 (wt. %)

Material	Y	Nd	Zn	Zr	Mn	Hf	TR	Mg
WE54	5.5	1.7	0.4	0.08	0.01	1.2	2.96	Bal

Laser irradiation was carried out by using a 500 watt Rofin pulsed Nd:YAG laser. A square beam shape having side length of 0.6mm was used to scan the surface of WE54 alloy. The position of the laser spot can be aligned by using Rofin control system. The experiments were performed in closed chamber with supply of nitrogen gas to reduce the oxygen formation on the surface of WE54 during the melting process. A vacuum tube was provided near the experiment area inside chamber to remove dust. The Nd:YAG laser parameters that were used to scan a (10 x 10) mm² surface area are listed in table 2. After laser surface irradiation, the surface was cleaned using ethanol.

Table 2: Laser processing parameters used in the study

Laser parameters (units)	Symbol	Value
Power density (x 10 ⁵ W/cm ²)	Pd	1.307, 2.770, 3.901
Frequency (Hz)	f	10000
Scanning speed (mm/s)	v	20
Overlap (%)	O	50
Hatching density (mm)	H	0.001
Pulse width (μs)	Pw	10
Focal length (mm)	F	152.5

The liquids used for the contact angle measurement are SBF (simulated body fluid) and deionized water. The chemical composition for 1000 ml of SBF is: Ultra-pure water - 750 mL, NaCl - 7.996 g, NaHCO₃ - 0.350 g, KCl - 0.224 g, (K₂HPO₄.3H₂O) - 0.228 g, (MgCl₂.6H₂O) - 0.305 g, (1 kmol/m³ HCl) - 40 cm³, CaCl₂ - 0.278 g, Na₂SO₄ - 0.071 g, (CH₂OH)₃CNH₂ - 6.057 g. The pH value of SBF is 7.4 at room temperature. After laser surface melting, the laser irradiated surface was subjected to wetting experiments. The contact angle measurement was performed at room temperature. An attension THETA AUTO-D tensiometer was used for the wetting measurements. It consists of a laser light, sample stage, micropipette system and a computer to control the experiments. 500μl volume of liquid was filled in the micropipette and 2μl volume was set for the sessile liquid droplet. The contact angle was measured 10 seconds after the liquid was dropped on the sample's surface. Five sets of contact angle were measured for each sample at different locations to validate the consistency of the data.

Laser irradiated surfaces were examined by JEOL 5600 LV Scanning electron microscope (SEM) and optical microscope (OM). Electron dispersive spectroscopy (EDS) was used to investigate the concentration of alloying elements on the laser irradiated surface. Taylor Hobson Profilometer was used to observe the surface morphology. 2 mm² surfaces were scanned with 2000 mm/s stylus speed. Cross section profile of laser irradiated surface and surface roughness were obtained from the profilometer. For the wettability analysis, 3D surface roughness parameter is necessary. Commonly used roughness parameters are Sq and its 2D counterpart Rq, which give the standard deviation of height.

3. Results and Discussion

3.1. Microstructure

Figure 2 a) shows the general microstructure of as-received WE54 which was observed by optical microscope. The as-received WE54 Mg alloy consists of α-Mg matrix and secondary phases including Y and Nd formed by precipitates along the grain boundaries as supported by the EDS and XRD observations. Analysis by Panalytical X'Pert HIGHSCORE Plus XRD analysis software showed that the secondary phases were Mg₂₄Y₅ and Mg₄₁Nd₅ phases. Figures 2 b) and c) show the general surface structure before and after laser surface irradiation of WE54. The chemical composition of the laser irradiated surface was changed as compared to the as-received WE54. The variation in the evaporation of Mg and enrichment of Y were obtained depending on the laser process parameters. When the laser power density of 1.307 x 10⁵ W/cm² was used, there was no significant change in the chemical composition of the laser irradiated surface. Figure 2 d) represents the surface structure created by using a power density of 1.307 x 10⁵ W/cm². Figures 2 e) and f) show the cellular microstructure melted by the power density of 2.77 x 10⁵ W/cm² and 3.90 x 10⁵ W/cm² respectively. Y element was increased from 5% to 12.15% and 13.43%,

whereas the concentration of Mg was reduced to 81.15% and 80.97% for laser power density of $2.77 \times 10^5 \text{ W/cm}^2$ and $3.90 \times 10^5 \text{ W/cm}^2$ respectively. The distribution of rare earth element along the grain boundaries was modified after the laser surface irradiation.

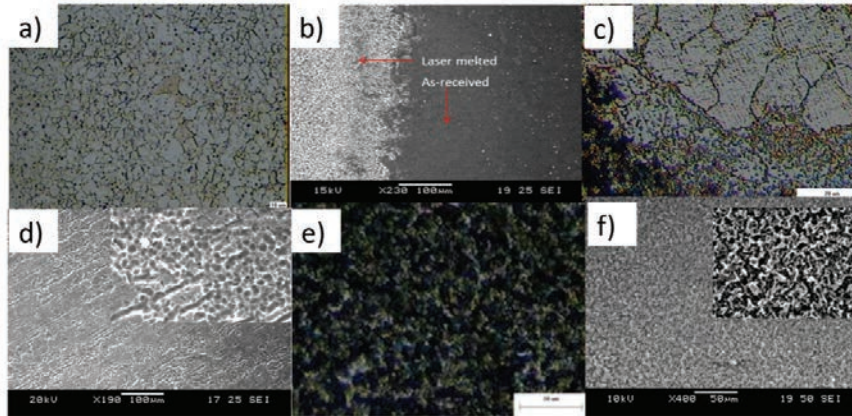


Figure 2: a) Microstructure of as-received WE54, b) and c) show the surface structure of WE54 before and after laser irradiation, d), e) and f) show the laser irradiated surface with power density of $1.307 \times 10^5 \text{ W/cm}^2$, $2.77 \times 10^5 \text{ W/cm}^2$ and $3.90 \times 10^5 \text{ W/cm}^2$ respectively.

3.2. Surface morphology

The surface roughness S_q (area root mean square height) of as-received and laser treated surface of WE54 with power density of $1.307 \times 10^5 \text{ W/cm}^2$, $2.77 \times 10^5 \text{ W/cm}^2$ and $3.90 \times 10^5 \text{ W/cm}^2$ were 0.170, 0.332, 0.241 and 0.532 μm respectively. The roughness value along with the standard deviation is listed in the table 3. Prior to measuring the roughness, the as-received WE54 was grounded by 2400 SiC paper, whereas the laser treated samples were cleaned with ethanol ultrasonic bath. It has been reported that the higher surface roughness with smaller grain size provides poor wettability [8]. The optimal combination of surface roughness, grain size and homogenous chemical composition of surface improves the wettability. When the laser power of 50 W was used, the surface was not melted properly because of insufficient power. Therefore the roughness of the surface was 0.332 μm which was high as compared to as-received and 100 W laser power irradiated surface roughness of WE54. With the increase in laser power, the surface roughness was increased. The surface roughness of 100W laser irradiated surface was lower than that of the 150 W laser irradiated surface. Ho et al. mentioned that the surface roughness of laser treated samples increased with an increase in the laser energy density [8], which is agreeable with our data.

3.3. Wetting characteristics

The contact angle measurement was performed in order to observe the wetting behavior of laser treated WE54 alloy. Figure 3 represents the contact angle photographs of as-received WE54, 50W, 100W and 150W laser treated surface of WE54 under DI water and SBF solution. The variations of contact angle are listed in table 3. By optimizing the laser processing parameters, the contact angle could be reduced from 81° to 43.10° and 41.03° in DI water and from 60.84° to 33.20° and 23.13° in SBF solution. Laser processing parameters affect the contact angle. Laser irradiated surface with 50W, 100W and 150W laser power have lower contact angle than that of the as-received WE54. At laser power density of $2.77 \times 10^5 \text{ W/cm}^2$, the minimum contact angles of 41.03° and 23.13° were observed for DI water and SBF respectively. Contact angle in SBF solution was smaller as compared to the contact angle of DI water. SBF solution consists of several ions representative of the composition of the human blood. These ions could play a role by reacting with the surface of the substrate. The surface roughness and microstructure have an influence on cell bioactivity. In this study, the moderate laser power density of $2.77 \times 10^5 \text{ W/cm}^2$ leading to a surface roughness of $0.241 \pm 0.033 \mu\text{m}$ produces a surface with better bio-wettability.

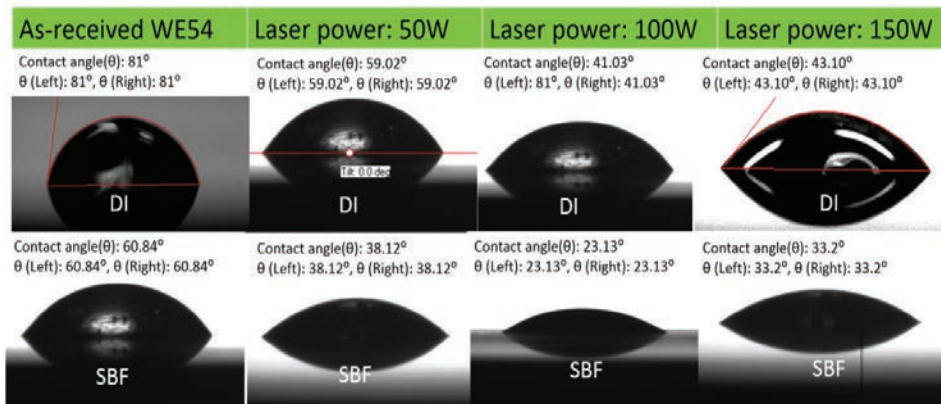


Figure 3: Wet angle measurement of as-received and laser treated surface of WE54 under deionised water (DI) and SBF solution

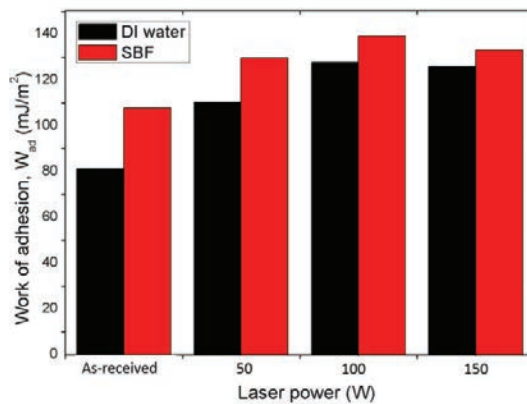


Figure 4: Adhesion intensities of DI water and SBF solution in different laser power

Table 3 : Summary of laser process parameters, adhesion energy, surface roughness and contact angle

Laser power density (105W/cm ²)	Roughness (Sq) μm	Adhesion energy (mJ/m ²)		Contact angle		Variation in contact angle (\pm)	
		DI water	SBF	DI water	SBF	DI water	SBF
As-received	0.170 \pm 0.002	81.18	107.87	81.00°	60.84°	3.00°	3.14°
1.307	0.332 \pm 0.031	110.27	129.59	59.02°	38.12°	2.56°	3.65°
2.770	0.241 \pm 0.033	127.71	139.22	41.03°	23.13°	4.15°	3.90°
3.901	0.532 \pm 0.047	125.95	133.22	43.10°	33.20°	5.50°	4.71°

Figure 4 represents the adhesion energies of DI water and SBF which were calculated by using the Young–Dupré equation (2). The surface tension (γ_{lv}) value of SBF was taken as $72.53 \pm 0.11 \text{ mJ/m}^2$ as reported elsewhere [18]. The work of adhesion of as-received WE54 was 81.18 mJ/m^2 and 107.87 mJ/m^2 in DI water and SBF solution respectively. The type of liquid used in the wetting experiment also has an influence in the measurement. The bio-

wettability of the material under SBF solution is very complex as there are several ions which are taking part during the process. The work of adhesion of SBF and DI water on laser treated WE54 50, 100 and 150W were 129.59, 139.22 and 139.22 mJ/m² and 110.27, 127.71, 125.95 mJ/m² respectively. The maximum adhesion energy of SBF was obtained when the contact angle was small. Small contact angle provides high surface and adhesion energy; hence improves the bio-wettability of WE54. Comparing the adhesion energy of SBF with that of DI water, the SBF has significantly better adhesion energy. The adhesion energy, contact angle and surface roughness data are summarized in the table 3.

4. Conclusion

Effective changes in the wettability characteristics of WE54 rare earth Mg alloy were found after Nd:YAG laser surface irradiation. The lowest contact angle of 23.13° was measured when wettability test was performed in SBF solution, with the surface roughness of $0.241 \pm 0.033 \mu\text{m}$. SBF significant adhesion intensity of 139.22 mJ/cm² was obtained when the laser power density was $2.770 \times 10^5 \text{ W/cm}^2$. Changes in the concentration of elements of WE54 alloy were observed by EDS. In the LSM process, Mg was evaporated during the melting process, and concentration of Y and Nd were increased. The changes in the laser treated surface chemical composition, microstructure and surface morphology were responsible for the improvement of wetting behavior. Therefore, wetting properties of WE54 in SBF solution was significantly improved which is beneficial for bio-applications.

Acknowledgement

Support by Singapore Institute of Manufacturing Technology (SIMTech) (project no. U12-M-015SU) and Nanyang Technological University (NTU) through the SINGA scholarship, Singapore, is gratefully acknowledged.

References

- [1] J. Lawrence and L. Li, "Wettability characteristics of carbon steel modified with CO₂, Nd:YAG, excimer and high power diode lasers," *Applied Surface Science*, vol. 154–155, pp. 664–669, 2/1/ 2000.
- [2] G. W. Critchlow, C. A. Cottam, D. M. Brewis, and D. C. Emmony, "Further studies into the effectiveness of CO₂-laser treatment of metals for adhesive bonding," *International Journal of Adhesion and Adhesives*, vol. 17, pp. 143–150, 5// 1997.
- [3] L. Hao, J. Lawrence, and L. Li, "The wettability modification of bio-grade stainless steel in contact with simulated physiological liquids by the means of laser irradiation," *Applied Surface Science*, vol. 247, pp. 453–457, 7/15/ 2005.
- [4] J. Lawrence, L. Hao, and H. R. Chew, "On the correlation between Nd:YAG laser-induced wettability characteristics modification and osteoblast cell bioactivity on a titanium alloy," *Surface and Coatings Technology*, vol. 200, pp. 5581–5589, 5/8/ 2006.
- [5] Z. Zhao, C. Wang, M. Li, L. Wang, and L. Kong, "The effects of pulsed Nd:YAG laser irradiation on surface energy of copper," *Applied Surface Science*, vol. 252, pp. 4257–4263, 4/15/ 2006.
- [6] Y. Guan, W. Zhou, and H. Zheng, "Effect of Nd: YAG laser melting on surface energy of AZ91D Mg alloy," *Surface Review and Letters*, vol. 16, pp. 801–806, 2009.
- [7] A. G. Demir, V. Furlan, N. Lecis, and B. Previtali, "Laser surface structuring of AZ31 Mg alloy for controlled wettability," *Biointerphases*, vol. 9, p. 029009, 2014.
- [8] Y.-H. Ho, H. D. Vora, and N. B. Dahotre, "Laser surface modification of AZ31B Mg alloy for bio-wettability," *Journal of biomaterials applications*, p. 0885328214551156, 2014.
- [9] P. A. Dearnley, "A brief review of test methodologies for surface-engineered biomedical implant alloys," *Surface and Coatings Technology*, vol. 198, pp. 483–490, 2005.
- [10] N. T. Kirkland, J. Lespagnol, N. Birbilis, and M. P. Staiger, "A survey of bio-corrosion rates of magnesium alloys," *Corrosion Science*, vol. 52, pp. 287–291, 2010.
- [11] R. Elin, "Assessment of magnesium status," *Clinical chemistry*, vol. 33, pp. 1965–1970, 1987.
- [12] <http://www.hhs.gov>.
- [13] T. F. da Conceição, N. Scharnagl, W. Dietzel, and K. U. Kainer, "Controlled degradation of a magnesium alloy in simulated body fluid using hydrofluoric acid treatment followed by polyacrylonitrile coating," *Corrosion Science*, vol. 62, pp. 83–89, 9// 2012.
- [14] G. Song, "Control of biodegradation of biocompatible magnesium alloys," *Corrosion Science*, vol. 49, pp. 1696–1701, 2007.
- [15] Y. Zhu, J. Xu, H. Sun, C. Hu, H. Zhao, B. Shao, et al., "Effects of aluminum exposure on the allergic responses and humoral immune function in rats," *BioMetals*, vol. 24, pp. 973–977, 2011/10/01 2011.
- [16] Y. Yuan and T. R. Lee, "Contact angle and wetting properties," in *Surface science techniques*, ed: Springer, 2013, pp. 3–34.
- [17] T. Young, "An Essay on the Cohesion of Fluids," *Philosophical Transactions of the Royal Society of London*, vol. 95, pp. 65–87, 1805.
- [18] M. Amaral, M. Lopes, J. Santos, and R. Silva, "Wettability and surface charge of Si 3 N 4–bioglass composites in contact with simulated physiological liquids," *Biomaterials*, vol. 23, pp. 4123–4129, 2002.